

**POLYNUCLEAR DITHIO- OR TRITHIOCARBONATE-BRIDGED
 COMPLEXES OF PALLADIUM(II) AND/OR PLATINUM(II).
 X-RAY STRUCTURE DETERMINATION OF
 $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pt}(\text{C}_6\text{F}_5)_2 \cdot \text{CH}_2\text{Cl}_2$ ***

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Summary

Trinuclear complexes $[(\text{L-L})\text{M}(\mu\text{-S}_2\text{CS})]_2\text{M}'(\text{C}_6\text{X}_5)_2$ with bridging CS_3^{2-} are obtained by the reaction of $(\text{L-L})\text{M}(\text{S}_2\text{CS})$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{L-L} = 1,2$ -bis(diphenylphosphino)ethane (dpe), 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane) with $\text{M}'(\text{C}_6\text{X}_5)_2(\text{OC}_4\text{H}_8)_2$ ($\text{M}' = \text{Pd}, \text{Pt}$; $\text{X} = \text{F}, \text{Cl}$). The reaction between $(\text{L-L})\text{M}(\text{S}_2\text{CO})$ and $\text{M}'(\text{C}_6\text{F}_5)_2(\text{OC}_4\text{H}_8)_2$ yields $(\text{L-L})\text{M}(\mu\text{-S}_2\text{CO})\text{M}'(\text{C}_6\text{F}_5)_2$, the first compounds containing a dithiocarbonate bridging ligand. New compounds have been characterized by IR and ^{31}P NMR spectroscopy, and the molecular structure of $[(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pt}(\text{C}_6\text{F}_5)_2$ established by a single crystal X-ray structure determination.

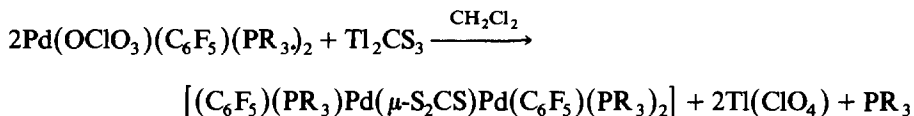
Introduction

We recently [1] described two syntheses of binuclear CS_3 -bridged complexes of palladium and/or platinum involving:

(a) Reaction of Ti_2CS_3 with perchlorate complexes of palladium(II), leading to

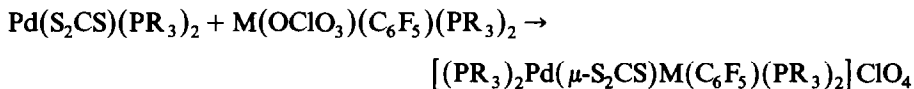
* Dedicated to Professor Rafael Usón on the occasion of his 60th birthday.

neutral homobinuclear species



(R = alkyl, aryl)

(b) Reaction of trithiocarbonato complexes of palladium(II) with perchlorato complexes of palladium(II) or platinum(II), leading to homo- or hetero-binuclear species, respectively:



(R = alkyl, aryl; M = Pd (in benzene as solvent), Pt (in CH_2Cl_2))

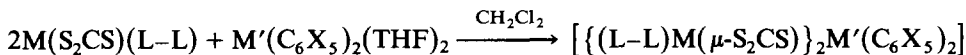
The synthesis [2] of precursors of the type $\text{M}'(\text{C}_6\text{X}_5)_2(\text{THF})_2$ (M' = Pd, Pt; X = F, Cl; THF = tetrahydrofuran) containing two weakly coordinated tetrahydrofuran groups allowed the isolation of trinuclear CS_3 -bridged compounds of the general formula $[(\text{L-L})\text{M}(\mu\text{-S}_2\text{CS})]_2\text{M}'(\text{C}_6\text{X}_5)_2$ (where M = Pd, Pt; M' = Pd, Pt; X = F, Cl; L-L = chelate diphosphine). We attempted to extend these observations to dithiocarbonate-bridged compounds (which, as far as we know, would be the first examples of bridging S_2CO), but in contrast to the trithiocarbonato complexes described above, the compounds isolated from the reaction between $\text{M}(\text{S}_2\text{CO})(\text{L-L})$ and $\text{M}'(\text{C}_6\text{F}_5)_2(\text{THF})_2$ are binuclear, $(\text{L-L})\text{M}(\mu\text{-S}_2\text{CO})\text{M}'(\text{C}_6\text{F}_5)_2$.

For the few known S_2CS -bridged compounds [1,3-9], the structures have usually been assigned from elemental analyses, IR and/or NMR spectra. Only in one case [9] has the trithiocarbonato bridge been confirmed by X-ray diffraction: $[\{(\text{CO})_4\text{Re}(\mu^3\text{-S}_2\text{SC})\}_2\{\text{Re}(\text{CO})_4\}_2]$. We report here the X-ray structure of $[\{(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CS})\}_2\text{Pt}(\text{C}_6\text{F}_5)_2]$.

Results and discussion

Trithiocarbonato complexes

Addition (2/1) of a trithiocarbonato complex of palladium(II) or platinum(II) to a dichloromethane solution of $\text{M}'(\text{C}_6\text{X}_5)_2(\text{THF})_2$ leads to the formation of the corresponding bridged trinuclear complexes



X = F; M = Pd; M' = Pd; L-L = dpe [1,2-bis(diphenylphosphino)ethane] (I) or dpb [1,4-bis(diphenylphosphino)butane] (II).

X = F; M = Pd; M' = Pt; L-L = dpe (III) or dpp [1,3-bis(diphenylphosphino)propane] (IV), dpb (V).

X = F; M = Pt; M' = Pd; L-L = dpe (VI)

X = F; M = Pt; M' = Pt; L-L = dpe (VII)

X = Cl; M = Pd; M' = Pd; L-L = dpe (VIII)

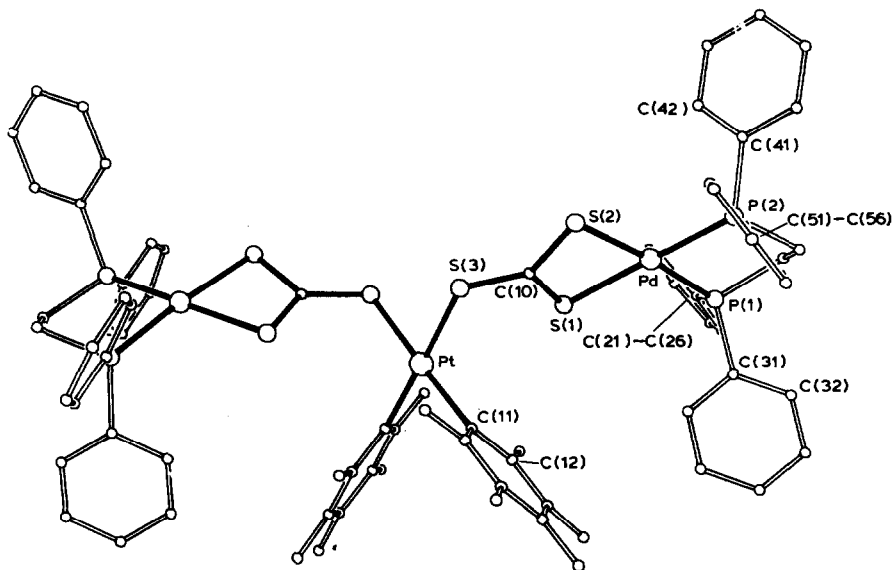


Fig. 1. The molecule of III in the crystal (radii arbitrary, H atoms omitted). The Pt atom lies on a crystallographic twofold axis at $0, y, -\frac{1}{8}$.

Whereas compounds III, IV, VI and VII precipitate out on formation, in all the other cases the solvent must be partially evaporated and diethyl ether added to precipitate the complexes which, however, are only slightly soluble once crystallized.

Yields and elemental analyses are given in Table 1.

The IR spectra (see Table 1) of the solids show one band in the $1050\text{--}900\text{ cm}^{-1}$ region assignable [1,3,5–7,9] to the CS_3 bridge, together with those expected for the neutral ligand. Complexes I–VII show two C_6X_5 absorptions [10] in the $800\text{--}760\text{ cm}^{-1}$ region (assignable [11] to the X-sensitive mode of the pentafluorophenyl groups), whereas complex VIII shows two bands in the $850\text{--}800\text{ cm}^{-1}$ region (assignable to the X-sensitive mode of the pentachlorophenyl group) and two more in the $620\text{--}600\text{ cm}^{-1}$ region [$\nu(\text{Pt}\text{--}\text{C})$] [11], thus confirming the *cis*-configuration of the two C_6F_5 or C_6Cl_5 moieties, respectively.

The molecular structures of the trinuclear complexes (I–VIII) were established by an X-ray diffraction study of compound III (see Fig. 1). Single crystals were grown by slow diffusion of two dichloromethane layers, each containing one of the starting materials.

The platinum atom lies on a crystallographic two-fold axis and is in an approximately *cis* square-planar environment, formed by one carbon of each C_6F_5 group and the terminal sulphurs of both the $(\text{SCS}_2)\text{Pd}(\text{dpe})$ moieties (r.m.s. deviation of ligand atoms from mean plane: 0.06 \AA). The Pt–C bond length, $2.072(6)\text{ \AA}$, is slightly greater than those in other compounds containing the *cis*-Pt(C_6F_5)₂ moiety: $1.972(12)$ and $1.963(12)\text{ \AA}$ in $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Br})_2\text{PdCOD}]_2$ [12], $2.017(2)\text{ \AA}$ in $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ [13] $2.0477(25)\text{ \AA}$ in $[(\text{C}_6\text{F}_5)_2\text{Pt}(\text{PhC}\equiv\text{CPh})_2]$ [14], $2.056(7)$ and $2.045(7)\text{ \AA}$ in $[(\text{C}_6\text{F}_5)_2\text{Pt}(\text{CO})(\text{SC}(\text{S})\text{PCy}_3)]$ [15]. The Pt–S(3) distance is $2.338(5)\text{ \AA}$.

TABLE I
ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES I–XII

Compound	Analyses (Found (calcd.)) (%)		Yield (%)	IR (ν in cm^{-1}) (Nujol mull)		^{31}P NMR (in CH_2Cl_2) δ (ppm)	$^1J(\text{Pt}-\text{P})$ (Hz)
	C	H		S_2CE vibr.	C_6X_5 vibr.		
$[(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pd}(\text{C}_6\text{F}_5)_2$ (I)	47.4 (47.6)	3.0 (2.9)	84	1020vs	1495vs, 1050s, 955vs, 785m, 775m	1440vs, 1105vs, 530s, 495m, 480m	52.82
$[(\text{dpp})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pd}(\text{C}_6\text{F}_5)_2 \cdot \text{CH}_2\text{Cl}_2$ (II)	47.8 (47.2)	3.1 (3.2)	52	1030vs	1490vs, 950vs, 780m, 770m	1430vs, 1095s, 515m, 510m, 500m, 465m	23.70
$[(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pt}(\text{C}_6\text{F}_5)_2 \cdot \text{CH}_2\text{Cl}_2$ (III)	43.9 (43.7)	2.6 (2.7)	60	1020vs	1495vs, 1050s, 960vs, 800m, 785m	1440vs, 1105s, 530m, 485m, 465m	51.67
$[(\text{dpp})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pt}(\text{C}_6\text{F}_5)_2$ (IV)	45.3 (45.8)	3.0 (2.9)	57	1025vs	1495vs, 955vs, 800m, 785m	1440vs, 1105s, 515s, 495m, 480m	^a
$[(\text{dpp})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pt}(\text{C}_6\text{F}_5)_2$ (V)	46.2 (46.4)	3.0 (3.1)	54	1030vs	1490vs, 955vs, 800m, 785m	1440vs, 1100s, 520m, 510m, 500m, 475m	22.55
$[(\text{dpe})\text{Pt}(\mu\text{-S}_2\text{CS})]_2\text{Pd}(\text{C}_6\text{F}_5)_2 \cdot \text{CH}_2\text{Cl}_2$ (VI)	42.0 (41.7)	2.6 (2.6)	75	1030vs	1500vs, 960vs, 790m, 780m	1440vs, 1110s, 530s, 490m, 485m	41.37
$[(\text{dpe})\text{Pt}(\mu\text{-S}_2\text{CS})]_2\text{Pt}(\text{C}_6\text{F}_5)_2 \cdot \text{CH}_2\text{Cl}_2$ (VII)	40.4 (39.9)	2.4 (2.5)	60	1020vs	1495vs, 1050s, 955vs, 795m, 785m	1430vs, 1100s, 530s, 485m	40.85
$[(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CS})]_2\text{Pd}(\text{C}_6\text{Cl}_5)_2 \cdot \text{CH}_2\text{Cl}_2$ (VIII)	41.6 (42.0)	2.6 (2.6)	79	1020vs	1330s, 1320s, 1290s 610d, 605d	1440vs, 1105m, 535s, 495m, 485m	52.90
$(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CO})\text{Pd}(\text{C}_6\text{F}_5)_2$ (IX)	45.3 (45.1)	2.3 (2.3)	45	1700vs, 1605m	1500vs, 1060s, 965vs, 785m, 775m	1440vs, 1100m, 525s, 490m	59.57
$(\text{dpe})\text{Pd}(\mu\text{-S}_2\text{CO})\text{Pt}(\text{C}_6\text{F}_5)_2$ (X)	41.4 (41.6)	2.4 (2.1)	20	1705vs, 1605w	1500vs, 1060s, 960vs, 800m, 790m sh	1435vs, 1105s, 520m, 485m	59.38
$(\text{dpe})\text{Pt}(\mu\text{-S}_2\text{CO})\text{Pd}(\text{C}_6\text{F}_5)_2$ (XI)	42.2 (41.6)	2.5 (2.1)	68	1720vs, 1610w	1500vs, 1060s, 960vs, 790m, 780m	1440vs, 1100s, 530m, 490m	42.37
$(\text{dpe})\text{Pt}(\mu\text{-S}_2\text{CO})\text{Pt}(\text{C}_6\text{F}_5)_2$ (XII)	38.1 (38.6)	2.0 (2.0)	54	1715vs, 1605w	1495s, 1060s, 960vs, 800m, 790m	1430vs, 1100m, 525s, 485m	44.23

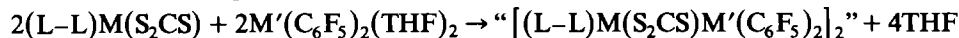
^a Insoluble.

The platinum atom is linked to each of the palladium atoms via a planar trithiocarbonate bridge (r.m.s. deviation 0.001 Å). The chelating nature of the bridge causes some distortion of the bond angles around C(10). The C–S bond lengths are appreciably longer for the chelating part of the trithiocarbonate than for the non-chelating; it is not clear whether this is general for CS_3^{2-} (there are few published structures of CS_3^{2-} complexes [9,18] and none with this coordination mode of bridging “ CS_2 ”, monodentate S) or is associated with the presence of electron-withdrawing C_6F_5 groups on the Pt atom.

The palladium atoms are in a distorted square-planar environment (r.m.s. deviation of 0.04 Å); the P(1)–Pd–P(2) bond angle is only 85.5° because of the chelating diphosphine. Similarly, the S(1)–Pd–S(2) angle is 74.8° , in agreement with that found for other PdSCS rings (73.8° in $[(\text{C}_6\text{F}_5)_2\text{Pd}(\text{S}_2\text{CPCy}_3)]$ [15], 73.8° in $[\text{Pd}(\text{S}_2\text{CNEt}_2)(\text{PPh}_3)\text{Cl}]$ [16], 74.5° in $\text{Pd}(\text{S}_2\text{CC}_6\text{H}_5)_2$ [17]) or for the S–Ni–S angle in $[\text{Ni}(\text{S}_2\text{CS})_2]^{2-}$ [18] (76.9°). The Pd–S bond length is similar to that found in the above-mentioned compounds. The angles between the ligand planes are Pd/Pt 113.8° , Pd/Pd' 103.2° .

The ^{31}P NMR spectra of complexes I–VIII (see Table 1) show a single signal (or a signal with the expected platinum satellites); this indicates that in solution all P nuclei are equivalent, probably due to rotation around the M–S bond. Long range $^5J(\text{Pt}–\text{P})$ couplings are not observed in compounds III–V and VII.

Since the structure found for compound III is closely related to that of $[\{(\text{CO})_4\text{Re}(\mu_3\text{-S}_2\text{CS})\}_2\{\text{Re}(\text{CO})_4\}_2]$ [9] (the only difference being that it presents a vacant site equivalent to that occupied by the one platinum centre), the reaction between equimolecular quantities of $(\text{L}–\text{L})\text{M}(\text{S}_2\text{CS})$ and $\text{M}'(\text{C}_6\text{F}_5)_2(\text{THF})_2$ was examined in the hope of obtaining tetranuclear compounds:

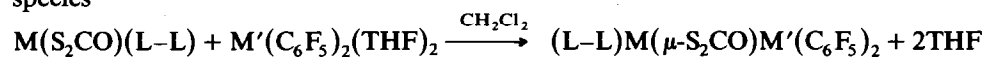


The solids thus obtained showed the expected analyses and IR spectra; however, their low solubility prevented further studies (such as NMR spectroscopy or molecular weight determinations) and their structures therefore remain uncertain.

Dicarbonato complexes

Fackler's method [19] was used for the synthesis of the mononuclear dithiocarbonato starting materials, since it yields only the *S,S'*-isomer, as confirmed by IR and NMR spectroscopy (see ref. 20).

Addition (1 : 1) of a dithiocarbonato complex of palladium(II) or platinum(II) to a dichloromethane solution of $\text{M}'(\text{C}_6\text{F}_5)_2(\text{THF})_2$ gives the corresponding binuclear species



L–L = dpe

M = Pd, M' = Pd (IX);

M = Pd, M' = Pt (X);

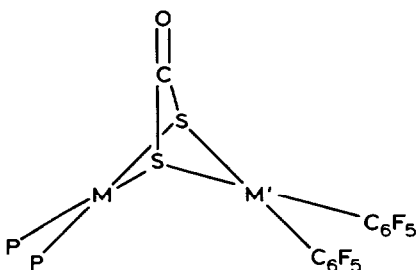
M = Pt, M' = Pd (XI);

M = Pt, M' = Pt (XII)

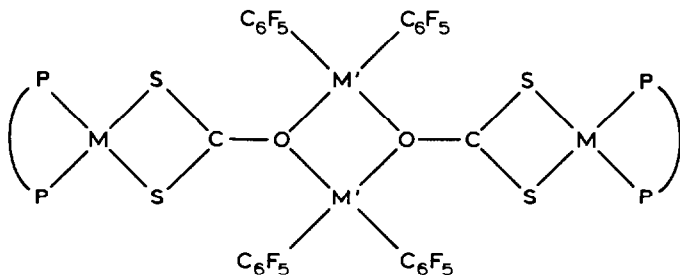
Compounds IX–XII are poorly soluble and decompose when their solutions are kept at room temperature, especially compound X, which could thus be isolated only in low yield.

The IR spectra (Table 1) of products IX–XII show, along with the bands expected for the neutral ligand L–L, two absorptions in the $800\text{--}760\text{ cm}^{-1}$ region (assignable [10] to the X-sensitive mode of the C_6F_5 group) thus confirming the *cis* geometry of the pentafluorophenyl moieties. In contrast to the mononuclear $(\text{L-L})\text{M}(\text{S}_2\text{CO})$ starting materials which, as expected [21], show two strong absorptions in the $1700\text{--}1600\text{ cm}^{-1}$ region (assigned to the $2\nu_{as}(\text{C-S})$ overtone and to the $\nu(\text{C=O})$ fundamental, both intense as a result of Fermi resonance), the lower energy band of the binuclear complexes is much less intense.

The ^{31}P NMR spectra (see Table 1) of these compounds show a single peak (IX, X) or a signal with the expected platinum satellites (XI, XII), so that all P nuclei must be equivalent in solution. A geometry consistent with these results could be



An alternative structure, analogous to that of the corresponding rhenium compound [9], would also be consistent with the analytical and spectroscopic results; however, since palladium(II) is a typical class *b* metal, this geometry seems less likely. Molecular weight determinations were prevented by the low solubility and stability of these dithiocarbonato complexes.



Experimental

All reactions were carried out at room temperature in solvents purified by standard procedures. The complexes $\text{M}'(\text{C}_6\text{X}_5)_2(\text{THF})_2$ [2], $\text{M}(\text{S}_2\text{CS})(\text{L-L})$ [1] and $\text{M}(\text{S}_2\text{CO})(\text{L-L})$ [19] were prepared as described elsewhere.

C and H analyses were performed with a Perkin–Elmer 240 B microanalyser. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer (over the range $4000\text{--}200\text{ cm}^{-1}$) using Nujol mulls between polyethylene sheets. The ^{31}P NMR spectra of dichloromethane solutions of the compounds were recorded on a Varian XL-200 spectrometer.

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR COMPOUND III

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Pt	0	6185.6(4)	-1666.7	53(1) ^a
Pd	1954(1)	5864(1)	-14.8(2)	51(1) ^a
P(1)	1469(2)	6354(2)	641(1)	56(1) ^a
P(2)	3342(2)	6023(2)	400(1)	55(1) ^a
S(1)	697(2)	5828(2)	-530(1)	59(1) ^a
S(2)	2367(2)	5412(2)	-723(1)	58(1) ^a
S(3)	1251(2)	5680(2)	-1510(1)	62(1) ^a
C(10)	1416(7)	5642(7)	-950(3)	47(2)
C(11)	1054(5)	7735(4)	-1489(2)	59(3)
C(12)	817	8212	-1131	67(3)
C(13)	1525	9257	-1013	84(3)
C(14)	2470	9824	-1253	88(4)
C(15)	2707	9346	-1611	75(3)
C(16)	1999	8302	-1729	67(3)
F(12)	-50(6)	7734(5)	-889(2)	92(4) ^a
F(13)	1316(7)	9748(6)	-685(2)	128(5) ^a
F(14)	3187(7)	10837(6)	-1144(3)	140(5) ^a
F(15)	3633(6)	9894(6)	-1839(3)	124(5) ^a
F(16)	2246(5)	7890(5)	-2068(2)	87(4) ^a
C(1)	2196(8)	6164(8)	1112(3)	69(3)
C(2)	3335(8)	6606(8)	952(3)	65(3)
C(22)	-313(6)	6034(5)	1125(2)	84(3)
C(23)	-1348	5413	1278	104(4)
C(24)	-1960	4380	1121	105(4)
C(25)	-1537	3969	810	97(4)
C(26)	-502	4590	657	84(4)
C(21)	110	5623	814	62(3)
C(32)	2373(6)	8394(7)	1016(2)	99(4)
C(33)	2753	9476	983	111(5)
C(34)	2609	9902	581	143(6)
C(35)	2084	9245	211	181(8)
C(36)	1704	8162	243	126(6)
C(31)	1848	7737	646	62(3)
C(42)	2469(5)	3822(6)	412(2)	80(3)
C(43)	2450	2898	546	101(4)
C(44)	3244	2951	828	97(4)
C(45)	4057	3928	976	100(4)
C(46)	4076	4852	842	81(3)
C(41)	3282	4799	560	55(3)
C(52)	5257(6)	7887(5)	232(2)	76(3)
C(53)	6224	8475	10	100(4)
C(54)	6552	7993	-310	92(4)
C(55)	5913	6922	-408	104(4)
C(56)	4946	6335	-187	87(4)
C(51)	4618	6817	134	57(2)
Cl	1021(21)	923(19)	1744(8)	353(11)

^a Equivalent isotropic *U* calculated from anisotropic *U*.

$\{[(L-L)M(\mu-S_2CS)]_2M'(C_6X_5)_2\}$ (I-VIII)

A solution of 0.5 mmol of $M(S_2CS)(L-L)$ in 15 ml of dichloromethane was added

TABLE 3
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR III

Pt-S(3)	2.338(5)	Pd-S(1)	2.357(4)
Pd-S(2)	2.342(4)	P(1)-Pd	2.281(4)
P(2)-Pd	2.275(4)	C(10)-S(1)	1.725(12)
C(10)-S(2)	1.720(13)	C(10)-S(3)	1.660(10)
C(11)-Pt	2.072(6)		
S(3)-Pt-C(11)	91.4(3)	S(3)-Pt-S(3a)	89.8(2)
C(11)-Pt-S(3a)	176.2(3)	C(11)-Pt-C(11a)	87.6(5)
P(1)-Pd-P(2)	85.5(2)	P(1)-Pd-S(1)	100.5(2)
P(2)-Pd-S(1)	171.6(2)	P(1)-Pd-S(2)	175.0(2)
P(2)-Pd-S(2)	99.0(2)	S(1)-Pd-S(2)	74.8(2)
Pd-P(1)-C(1)	106.7(5)	Pd-P(1)-C(21)	118.4(4)
C(1)-P(1)-C(21)	104.5(5)	Pd-P(1)-C(31)	112.8(4)
C(1)-P(1)-C(31)	106.6(5)	C(21)-P(1)-C(31)	107.0(5)
Pd-P(2)-C(2)	107.7(5)	Pd-P(2)-C(41)	115.9(3)
C(2)-P(2)-C(41)	103.0(6)	Pd-P(2)-C(51)	114.7(4)
C(2)-P(2)-C(51)	108.9(5)	C(41)-P(2)-C(51)	105.7(5)
Pd-S(1)-C(10)	85.9(5)	Pd-S(2)-C(10)	86.5(4)
Pt-S(3)-C(10)	110.7(5)	S(1)-C(10)-S(2)	111.9(6)
S(1)-C(10)-S(3)	125.9(8)	S(2)-C(10)-S(3)	122.2(7)

Symmetry operator: (a) $-x, y-x, -(1/3)-z$

to 0.25 mmol of $M(C_6X_5)_2(THF)_2$ in 15 ml of dichloromethane. In the case of complexes III, IV, VI and VII, the precipitated solid was filtered off after 3 h stirring and washed with 2 ml of dichloromethane, whereas in the case of compounds I, II, V and VIII it was necessary to evaporate the solvent to 5 ml and add 10 ml of ether to precipitate the solids. Yields are given in Table 1.

[(L-L)M(μ -S₂CO)M'(C₆F₅)₂] (IX-XII)

A solution of 0.25 mmol of $M(S_2CO)(L-L)$ in 25 ml of dichloromethane was added to 0.25 mmol of $M'(C_6F_5)_2(THF)_2$ in dichloromethane. After 10 min stirring the solvent was evaporated to 5 ml then cooled to $-20^\circ C$. The solid was filtered off and washed with 2×2 ml of cold dichloromethane. Yields are given in Table 1.

Crystal structure determination of III

Crystal data. $C_{66}H_{48}F_{10}P_4Pd_2PtS_6 \cdot CH_2Cl_2$, $M = 1840$. Trigonal, $P3_221$, a 14.636(2), c 29.237(4) Å, U 5424 Å³, $Z = 3$, D_x 1.69 g cm⁻³, $\lambda(Mo-K_\alpha)$ 0.71069 Å $\mu(Mo-K_\alpha)$ 2.8 mm⁻¹, $F(000) = 2706$.

Data collection and reduction. Stoe-Siemens four-circle diffractometer, monochromated Mo- K_α radiation, $2\theta_{max}$ 55°; 9127 reflections measured in profile-fitting mode [22], 7401 unique, 5413 with $F > 4\sigma(F)$ used for all calculations. Absorption correction based on ψ -scans; crystal size 0.5 \times 0.5 \times 0.5 mm, transmissions 0.74–0.89. Cell constants refined from 2θ values of 72 reflections in the range 20–23°.

Structure solution and refinement. Heavy-atom method, refinement on F to R 0.059, R_w 0.053. Pt, Pd, P, S and F atoms anisotropic; aromatic rings constrained to regular hexagons with C–C 1.395 Å, C–H (where applicable) 0.96 Å, C–C–C and C–C–H angles 120°; CH₂ groups with C–H 0.96 Å, H–C–H 109.5°; $U(H) = 1.2 U_{eq}(C)$. Disordered solvent molecule included in refinement as isotropic Cl.

Weighting scheme $w^{-1} = \sigma^2(F) + 0.0004F^2$; 181 parameters. Absolute structure [23] by η refinement [24]; $\eta = +1.02(2)$. Final atom coordinates and derived dimensions are given in Tables 2 and 3*.

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* Further crystallographic data (complete bond lengths and angles, H atom coordinates, temperature factors, structure factors) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D7514 Eggenstein-Leopoldshafen 2 (F.R.G.). Please quote reference no. CSD 51917, the names of the authors and the title of the paper.